NUCLEAR DYNAMICS IN DEGENERATE STATES OF ALKALI TRIMERS - HIGH RESOLUTION SPECTROSCOPY AND ACCURATE QUANTUM CALCULATIONS

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Molecules with strong vibronic coupling and large amplitude motions can not be characterized by the parameters of simple models for MO structure, geometric structure, normal modes and rigid rotation. Even for small molecules their spectra are highly complex and require very accurate calculations for assignment and reduction to an adequate model for structure and nuclear motion. This is exemplified for Alkali trimers in electronically degenerate states which provide text book examples of Jahn-Teller distortion and geometric phase.

Rotationally resolved spectra of the electronic systems $A^2E'' \leftarrow X^2E'$ of Li_3 and Na_3 have been recorded by sub-Doppler laser spectroscopy using RTPI and OODR techniques. The complex spectra could be analyzed and assigned by reference to theoretical spectra based on *ab initio* calculations for potential energy surfaces, spin densities and rovibrational states. For the latter a single-surface adiabatic treatment with geometric phase π proved adequate. Transition energies are correct to about 50 cm^{-1}, vibrational energies to about 2 cm^{-1}, rotational constants to 1% and hf splittings are reproduced to within 3%. Various rovibronic couplings produce complex level patterns which could be accurately represented by an effective pseudo/rotation Hamiltonian based on the superposition of three equivalent local vibrators in the C_{2v} potential minima. Its rotational and coupling constants directly provide structural information. A large variety of hfs line profiles is shown to emerge from the rovibronic couplings and in particular from the magnetic in-equivalence connected to vanishing Coriolis coupling.

H.v. Busch, V. Dev, H.-A. Eckel, S. Kasahara, J. Wang, W. Demtroeder, P. Sebald and W. Meyer, Phys. Rev. Lett. **81**, 4584 (1998).
H.G. Kraemer, M. Keil, C.B. Suarez, W. Demtroeder and W. Meyer, Chem. Phys. Lett. **299**, 212 (1999).
M. Keil, H.G. Kraemer, A. Kudell, M.A. Baig, J. Zhu, W. Demtroeder and W. Meyer, J. Chem. Phys. **113**, 7414 (2000).
W. Meyer, M. Keil, M.A. Baig, J. Zhu, and W. Demtroeder, J. Chem. Phys. **115**, 2590 (2001) and refs. therein.